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Title of the Invention: OPTICAL INFORMATION RECORDING  
MEDIUM, RECORDING/REPRODUCING METHOD FOR THE SAME,  
AND OPTICAL INFORMATION RECORDING/REPRODUCING  
SYSTEM UTILIZING THE SAME

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is a true translation to the best of my knowledge and belief of Japanese  
Patent Application No. Heisei 11-362948 (Date of Application: December  
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[TITLE OF THE INVENTION] OPTICAL INFORMATION RECORDING  
MEDIUM AND RECORDING/REPRODUCING METHOD FOR THE SAME  
[CLAIMS]

[Claim 1] An optical information recording medium, comprising on a substrate one or more information layers as a multi-layer film including recording layers, respectively, each recording layer containing a material that can exhibit a reversible transition between a crystalline state and an amorphous state in response to irradiation with a laser beam as a main component, wherein, in at least one of the recording layers, said material has an energy gap ranging from 0.9 eV to 2.0 eV in the amorphous state, wherein the information layer including the recording layer that contains said material as a main component thereof has a transmittance of not less than 30% when irradiated with a laser beam having a wavelength ranging from 300 nm to 450 nm.

[Claim 2] The optical information recording medium according to claim 1, wherein, in at least two of the information layers, the recording layers exhibit the reversible transition between the crystalline state and the amorphous state in response to irradiation with a laser beam that is incident on said material of the recording layers from a same direction.

[Claim 3] The optical information recording medium according to claim 2, wherein in at least one close to an incident side of the laser beam out of two of the information layers, said material as the main component of the recording layer of said information layer has an energy gap ranging from 0.9 eV to 2.0 eV in the amorphous state, and said information layer has a transmittance of not less than 30% when irradiated with a laser beam having a wavelength ranging from 300 nm to 450 nm.

[Claim 4] The optical information recording medium according to claim 1, wherein a reflectance  $R_c$  of said recording layer with respect to the laser beam when said recording layer is in the crystalline state is higher than a reflectance  $R_a$  thereof with respect to the laser beam when said recording layer is in the amorphous state.

[Claim 5] The optical information recording medium according to claim 1, wherein a light absorptance  $A_c$  of said recording layer with respect to the laser beam when the recording layer is in the crystalline state is greater than a light absorptance  $A_a$  thereof when said recording layer is in the

amorphous state.

[Claim 6] The optical information recording medium according to claim 1, wherein, throughout a wavelength range from 350 nm to 450 nm, the recording layer satisfies a relationship expressed as  $n_a > 2.5$ ,  $n_c > 2.5$  and  $k_a < 2.0$

where  $n_c$  represents a refractive index of said material in the crystalline state,  $n_a$  represents a refractive index of said material in the amorphous state, and  $k_a$  represents an extinction coefficient of said material in the amorphous state.

[Claim 7] The optical information recording medium according to claim 1, wherein said recording layer contains Se, and a content of Se in said recording layer is not less than 20 at% and not more than 60 at%.

[Claim 8] The optical information recording medium according to claim 1, wherein said recording layer contains Te and X, X representing at least one element selected from the group consisting of In, Al, Ga, Zn, and Mn, wherein a content of Te in said recording layer is between 20 at% and 60 at%, and a content of X therein is between 20 at% and 50 at%.

[Claim 9] The optical information recording medium according to claim 7 or 8, wherein said recording layer further contains at least one element selected from the group consisting of Al, Ga, In, Si, Ge, Sn, Sb, Bi, Sc, Ti, Nb, Cr, Mo, Co, Cu, Ag, Au, Pd, N, and O.

[Claim 10] The optical information recording medium according to claim 1, wherein the information layer including said recording layer has a crystallization promoting layer that is provided on at least one side of said recording layer so as to be in contact with a surface of said recording layer on the side.

[Claim 11] The optical information recording medium according to claim 10, wherein the crystallization promoting layer contains N.

[Claim 12] The optical information recording medium according to claim 1, wherein said recording layer has a thickness ranging from 1 nm to 25 nm.

[Claim 13] A method for recording, reproducing, or erasing information using an optical information recording medium comprising on a substrate one or more information layers as a multi-layer film including recording layers, respectively, each recording layer containing a material that can exhibit a reversible transition between a crystalline state and an amorphous state in response to irradiation with a laser beam as a main component,

wherein, in at least one of the recording layers, said material has an energy gap ranging from 0.9 eV to 2.0 eV in the amorphous state, wherein the information layer including the recording layer that contains said material as a main component thereof has a transmittance of not less than 30% when irradiated with a laser beam having a wavelength ranging from 300 nm to 450 nm; the recording/reproduction method for the optical information recording medium, comprising:

when an amorphous-state-producing power level that causes only a portion of the recording layer irradiated with a laser beam converged to a microspot by an optical system to reversibly change from the crystalline state to the amorphous state is given as P1, a crystalline-state-producing power level thereof that causes a portion irradiated with the laser beam to reversibly change from the amorphous state to the crystalline state is given as P2, and a reproduction power level that is lower than both of P1 and P2, at which the laser irradiation does not affect an optical state of the recording layer but allows a sufficient reflectance to be obtained for reproduction of information is given as P3,

while the wavelength of the laser beam is set to range from 300 nm to 450 nm,

recording and erasing the information by the laser beam whose power level is modulated between P1 and P2 and reproducing the information by the laser beam whose power level is at P3.

#### [DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical field to which the invention pertains]

The present invention relates to an optical information recording medium that allows information to be recorded/reproduced and rewritten thereto/therefrom at a high density and at a high speed with an optical means such as a laser beam applied thereto, as well as to a recording/reproducing method applied to the same.

[0002]

[Prior Art]

Optical information recording media such as magneto-optical recording media and phase-change recording media have been known as recording media that allow mass-storage and high-speed information recording and information rewriting. Such an optical information

recording medium utilizes, for information recording, changes caused in optical characteristics of its recording material by partial irradiation with a laser beam. For instance, a magneto-optical recording medium utilizes, for information recording, different rotational angles of polarization planes in reflected light caused by different magnetization states. A phase-change recording medium utilizes, for information recording, a phenomenon in which a reflected light quantity with respect to light with a specific wavelength differs between when the medium is in a crystalline state and when it is in an amorphous state. The phase-change recording medium is capable of erasing information and overwriting information simultaneously by modulating an output power of a laser beam, thereby allowing information signals to be rewritten at a high speed readily.

[0003]

Such optical recording media have significant merits such as random accessibility in response to needs and excellent portability, and hence has more significance in the highly information-oriented society. They are used, or considered for use, for various purposes and in various fields: for instance, for recording and storage of personal data and video information by means of computers, in medical fields, in academic researches, as a portable recording medium for use in a digital video recorder, for replacement of video tape recorders for home use. A typical example of an article in which a phase-change recording material is used is a DVD-RAM, which is randomly accessible. This is a disk-form medium with a diameter of 120 mm that has a storage capacity of 2.6 GB on one surface (5.2 GB in the case of a lamination type). Now further expansion of the storage capacity (high densification) and further increase in speed are demanded as to these optical information recording media, in response to improvement in performances of applications and image information.

[0004]

Examples of means to achieve high densification that have been proposed conventionally include laser with a shorter wavelength and a higher numerical aperture for a laser beam. Each of these makes it possible to decrease a minimum size of a laser beam spot, thereby enabling high densification of recording in a direction parallel with the laser scanning direction.

[0005]

As another technique for achieving high densification, a so-called multi-layer recording medium technique has been proposed, in which a medium having two or more information layers that are provided on top of the other with a transparent separation layer interposed therebetween is used and all the information layers are accessible with a laser from only one side. This technique can increase the recording density in the incident direction of a laser beam and increase the capacity of the medium as a whole when considered three dimensionally.

[0006]

[Problem to be solved by the invention]

Conventionally, a typical emission wavelength of a laser beam has been obtained at a red range (for instance, a specific value in a range of 650 nm to 860 nm), and a laser at a wavelength in this range was low-cost and available readily. Therefore, to realize an optical information recording medium for use with this a laser, a recording material has been developed that exhibits adequate light absorption with respect to the red wavelength range and exhibits a significant change in the optical characteristics.

[0007]

In these days, however, lasers at wavelengths in a blue range (for instance, wavelengths of 300 nm to 450 nm) that enables higher density recording have been developed, even to a merchandise level in terms of technologies. Accordingly, a recording material having an excellent optical characteristic in the blue wavelength range is required, but the fact that a recording material optimized for the conventional red wavelength range does not necessarily achieve excellent characteristics in the blue wavelength range has become known.

[0008]

When a recording material with light absorption characteristics optimized for the red wavelength range is used as a recording layer in the case of constructing a light-transmitting-type information layer on a side closer to the laser-incident side in the medium constituting the multi-layer recording medium capable of recording and reproducing from one side, in particular, the layer exhibits increased absorption of laser in the blue wavelength range, thereby making it difficult to improve a transmittance of the information layer. On the other hand, an attempt to improve the transmittance of the information layer makes it difficult to achieve a



sufficiently great difference between optical characteristics of the information layer.

[0009]

An object of the present invention is to solve the aforementioned problems, and to provide an optical information recording medium having an information layer with desirable light absorption characteristics with respect to light in the blue wavelength range. More specifically, an object of the present invention is to provide an optical information recording medium having a light-transmitting-type information layer that exhibits a high light transmittance with respect to light in the blue wavelength range and that provides a high contrast. Furthermore, another object of the present invention is to provide a recording/reproducing method applicable to the foregoing optical information recording medium.

[0010]

[Means for solving problem]

In order to achieve the objects described above, according to the present invention, in an optical information recording medium including on a substrate one or more information layers as a multi-layer film including recording layers, respectively, each recording layer containing a material that can exhibit a reversible transition between a crystalline state and an amorphous state in response to irradiation with a laser beam as a main component, the above-noted material is set to have an energy gap ranging from 0.9 eV to 2.0 eV in the amorphous state in at least one of the recording layers. This allows desirable light absorption characteristics to be obtained even in the case where a laser beam with a shorter wavelength than conventionally is used, and therefore, makes it possible to provide an optical information recording medium that exhibits excellent recording characteristics in the short wavelength range. Incidentally, in the present specification, "main component" indicates a content of not less than 50 atomic percent (at%).

[0011]

This optical information recording medium particularly is suitable for recording/reproducing information by a laser beam with a wavelength ranging from 300 nm to 450 nm.

[0012]

Furthermore, in the optical information recording medium of the

present invention, the information layer including the recording layer that contains the material as a main component thereof has a transmittance of not less than 30%, preferably not less than 50%, when irradiated with a laser beam having a wavelength in the foregoing range. With this configuration, in the case where, for instance, two information layers are provided, recording/reproduction of information is achieved only by irradiation with a laser beam in the same direction (usually from the substrate side), even with respect to the farther information layer from the light-incident side as well. It should be noted that here, more specifically, the transmittance with respect to the laser beam is determined according to a transmittance in the case where information is recorded in the information layer.

[0013]

In other words, the optical information recording medium of the present invention preferably has at least two of the information layers, each including a recording layer that can exhibit a reversible transition between the crystalline state and the amorphous state in response to irradiation with a laser beam that is incident from the same direction. Thus, by providing the optical information recording medium in a so-called multi-layer recording medium form (a configuration in which a plurality of information layers are provided), the recording capacity of the medium can be increased efficiently.

[0014]

According to the present invention, as compared with a case where a conventional recording material for the red wavelength range is used, optimization of a light absorption of the medium is facilitated even with respect to a short wavelength range. Therefore, it is possible to allow the medium to have a higher light transmittance and a greater contrast. Consequently, it is possible to make the light transmittance of the information layer higher as above, thereby providing a high-performance multi-layer recording medium.

[0015]

In the case of a multi-layer recording medium, more specifically, in the case where the optical information recording medium includes two information layers, in at least one of the information layers close to a laser beam incident side, the material as the main component of the recording

layer in the information layer preferably exhibits an energy gap ranging from 0.9 eV to 2.0 eV in the amorphous state. Furthermore, the foregoing information layer preferably has a transmittance of not less than 30% when irradiated with a laser beam with a wavelength ranging from 300 nm to 450 nm.

[0016]

In the foregoing optical information recording medium, a reflectance  $R_c$  of the recording layer with respect to the laser beam when the recording layer is in the crystalline state preferably is higher than a reflectance  $R_a$  thereof with respect to the laser beam when the recording layer is in the amorphous state ( $R_c > R_a$ ). In this preferable example, a higher transmittance is obtained while a high light absorptance is maintained.

[0017]

Furthermore, in the above-described optical information recording medium, a light absorptance  $A_c$  of the recording layer with respect to the laser beam when the recording layer is in the crystalline state preferably is higher than a light absorptance  $A_a$  thereof when the recording layer is in the amorphous state ( $A_c > A_a$ ). This causes deformation of recording marks to be minimized even in the case where overwriting recording is carried out, thereby allowing excellent recording characteristics to be obtained.

[0018]

Furthermore, in the above-described optical information recording medium, with respect to the wavelength range of 350 nm to 450 nm, the recording layer preferably satisfies the relationship expressed as  $n_a > 2.5$ ,  $n_c > 2.5$  and  $k_a < 2.0$ , where  $n_c$  represents a refractive index in the crystalline state,  $n_a$  represents a refractive index in the amorphous state, and  $k_a$  represents an extinction coefficient in the amorphous state. This makes it easier to provide a medium with a high transmittance and a great optical characteristic difference.

[0019]

More specifically,  $k_c$  (extinction coefficient in the crystalline state) and  $k_a$  preferably satisfy relationship in that an absolute value of a difference between  $k_c$  and  $k_a$  ( $|k_c - k_a|$ ) is not less than 0.5. This makes it easier to obtain a greater optical characteristic difference. Furthermore,  $n_a$  and  $n_c$  preferably satisfy the relationship expressed as  $n_a - n_c \leq 1.0$ . In

this preferable example, the relationship of  $A_c > A_a$  is established more readily, and this causes deformation of recording marks to be minimized even in the case where overwriting recording is carried out, thereby allowing excellent recording characteristics to be obtained.

[0020]

The recording layer preferably contains a phase changeable material containing at least one of Te and Se. This makes it possible to obtain a greater optical characteristic difference between the crystalline state and the amorphous state easily.

[0021]

In the case where the recording layer contains Se, a content of Se in the recording layer preferably is not less than 20 at% and not more than 60 at%, more preferably, not more than 50 at%. This preferable example allows an energy gap in an optimal range of 0.9 eV to 2.0 eV to be obtained readily, thereby making it possible to provide a recording material that exhibits high stability when in the amorphous state and that has a high crystallization kinetic.

[0022]

In the case where the recording layer contains Te, the recording layer preferably contains X (X represents at least one element selected from In, Al, Ga, Zn, and Mn) at the same time. This makes it possible to obtain an energy gap of 0.9 eV to 2.0 eV easily. Furthermore, a content of Te in the recording layer preferably is between 20 at% and 60 at%. A content of X therein preferably is between 20 at% and 50 at%. In the case where the contents are in the foregoing ranges, it is possible to provide a recording material that exhibits high stability when in the amorphous state and that has a high crystallization kinetic.

[0023]

In the case where the recording layer contains at least one of Te and Se, the recording layer preferably further contains at least one element selected from Al, Ga, In, Si, Ge, Sn, Sb, Bi, Sc, Ti, Nb, Cr, Mo, Co, Cu, Ag, Au, Pd, N, and O. The recording layer to which such a material is added exhibits improved stability in the amorphous state, a higher crystallization kinetic, and improved repetitive recording characteristics.

[0024]

In the above-described optical information recording medium, the

information layer preferably includes a crystallization promoting layer that is provided on at least one side of the recording layer so as to be in contact with a surface of the recording layer on the side. Furthermore, the crystallization promoting layer particularly preferably contains N. The crystallization promoting layer allows a time required for crystallization of the recording material to be shortened, thereby ensuring a higher-speed recording.

[0025]

In the foregoing optical information recording medium, the recording layer preferably has a thickness ranging from 1 nm to 25 nm. This makes it possible to provide an information layer that has excellent recording characteristics, a high transmittance, and minimum of adjacent erasure.

[0026]

Furthermore, the present invention provides a method for recording, reproducing or erasing information with use of the optical information recording medium described above. This method is characterized by, when an amorphous-state-producing power level that causes only a portion of the recording layer irradiated with a laser beam converged to a microspot by an optical system to reversibly change from the crystalline state to the amorphous state is given as P1, a crystalline-state-producing power level thereof that causes a portion irradiated with the laser beam to reversibly change from the amorphous state to the crystalline state is given as P2, and a reproduction power level that is lower than both of P1 and P2, at which the laser irradiation does not affect an optical state of the recording layer but allows a sufficient reflectance to be obtained for reproduction of information is given as P3, while the wavelength of the laser beam is set to range from 300 nm to 450 nm, recording and erasing the information by the laser beam whose power level is modulated between P1 and P2 and reproducing the information by the laser beam whose power level is at P3. This enables recording of information to the optical information recording medium at a high density, and reproduction of the information therefrom.

[0027]

[Mode for carrying out the invention]

The following description will depict a preferred embodiment of the present invention, while referring to the drawings.

An example of a layer configuration of an optical information

recording medium is shown in FIG. 1. In this configuration example, a first protective layer 2, a first interface layer (crystallization promoting layer) 3, a recording layer 4, a second interface layer (crystallization promoting layer) 5, a second protective layer 6, and a reflection layer 7 are laminated on a substrate 1 in the stated order.

[0028]

The configuration of the optical information recording medium of the present invention, however, is not limited to the configuration shown in FIG. 1 as long as a multi layer including the recording layer 4 is formed as the information layer on the substrate 1. For instance, in FIG. 1, another layer may be provided between the protective layer 6 and the reflection layer 7; the reflection layer 7 may be composed of two reflection layers; another layer may be provided between the substrate 1 and the protective layer 2; the protective layer 2 entirely may be replaced with the interface layer 3; the protective layer 6 entirely may be replaced with the interface layer 5; the interface layer 3 and/or the interface layer 5 may be omitted; or, other layers may be provided on a side of the reflection layer 6 to which a laser beam is incident and on an opposite side of the same.

[0029]

The substrate 1 preferably is made of a resin such as polycarbonate or PMMA, or glass, and is provided with guide grooves for guiding the laser beam. It should be noted that it is preferable to use a material that causes the substrate 1 to have a minimum of light absorption with respect to laser beam wavelengths used for signal recording/reproduction.

[0030]

The protective layers 2 and 6 are provided mainly with a view to protecting the recording material and allowing adjustment of optical characteristics, such as allowing effective light absorption at the recording layer. As materials of the protective layers 2 and 6, materials that allow the foregoing objects to be achieved are utilized. Examples of such materials include: sulfides such as ZnS; selenides such as ZnSe; oxides such as Si-O, Al-O, Ti-O, Ta-O, and Zr-O; nitrides such as Ge-N, Cr-N, Si-N, Al-N, Nb-N, Mo-N, Ti-N, Zr-N, and Ta-N; nitrogen oxides such as Ge-O-N, Cr-O-N, Si-O-N, Al-O-N, Nb-O-N, Mo-O-N, Ti-O-N, Zr-O-N, and Ta-O-N; carbides such as Ge-C, Cr-C, Si-C, Al-C, Ti-C, Zr-C, and Ta-C; fluorides such as Si-F, Al-F, and Ca-F; other dielectrics; and suitable combinations of these (for

instance  $\text{ZnS-SiO}_2$ ).

[0031]

The interface layers 3 and 5 serve for protection of the recording layer, for instance, for prevention of oxidation, corrosion, and deformation of the recording layer 4. At the same time, since the interface layers 3 and 5 are provided in such a manner as to be in contact with the recording layer 4, they play important roles in improving repetitive recording characteristics by preventing mutual diffusion of atoms constituting the recording layer 4 and atoms constituting the protective layers 2 and 6, and in improving erasure characteristics by promoting crystallization of the recording layer 4. The interface layers 3 and 5 may be provided only at one of the interfaces of the recording layer 4. However, to sufficiently achieve the foregoing effect, they preferably are provided on both sides of the recording layer 4. In the case where the recording layer 4 is relatively thin, this tends to hinder crystallization of the recording layer, but provision of the interface layers 3 and 5 on both the sides of the recording layer 4 can promote the crystallization of the recording layer, thereby ensuring a high erasure performance.

[0032]

Incidentally, components contained in the interface layers 3 and 5 possibly may be diffused in the recording layer 4 as information recording is repeatedly carried out. Considering this, it is preferable that materials hardly hindering optical changes in the recording layer 4 are used to form the interface layers 3 and 5. The interface layers 3 and 5 may be made of the materials suggested above as the materials for the protective layers 2 and 6, and the following materials may be used as a main component to form the interface layers 3 and 5: nitrides such as  $\text{Ge-N}$ ,  $\text{Cr-N}$ ,  $\text{Si-N}$ ,  $\text{Al-N}$ ,  $\text{Nb-N}$ ,  $\text{Mo-N}$ ,  $\text{Ti-N}$ ,  $\text{Zr-N}$ , and  $\text{Ta-N}$ ; nitrogen oxides such as  $\text{Ge-O-N}$ ,  $\text{Cr-O-N}$ ,  $\text{Si-O-N}$ ,  $\text{Al-O-N}$ ,  $\text{Nb-O-N}$ ,  $\text{Mo-O-N}$ ,  $\text{Ti-O-N}$ ,  $\text{Zr-O-N}$ , and  $\text{Ta-O-N}$ ; oxides such as  $\text{Si-O}$ ,  $\text{Al-O}$ ,  $\text{Ti-O}$ ,  $\text{Ta-O}$ , and  $\text{Zr-O}$ ; carbides such as  $\text{Ge-C}$ ,  $\text{Cr-C}$ ,  $\text{Si-C}$ ,  $\text{Al-C}$ ,  $\text{Ti-C}$ ,  $\text{Zr-C}$ , and  $\text{Ta-C}$ ; fluorides such as  $\text{Si-F}$ ,  $\text{Al-F}$ , and  $\text{Ca-F}$ ; other dielectrics; and suitable mixtures of these.

[0033]

A dense film often can be obtained as the interface layer in the case where a nitride or a nitrogen oxide is used as the main component, and such a film is preferable since the foregoing effects are obtained remarkably. It

should be noted that a sulfide or a selenide may be mixed in the interface layer according to conditions, but in this case, it is necessary to select compositions and forming conditions of the interface layers 3 and 5 so that sulfur should not be diffused in the recording layer 4.

[0034]

The interface layers 3 and 5 preferably have a thickness of not less than 1 nm each. This is because the effect of preventing diffusion of atoms between the protective layers 2 and 6 and the recording layer 4 deteriorates in the case where the film thickness is less than 1 nm.

[0035]

The reflection layer 7 preferably is made of a metal such as Au, Ag, Cu, Al, Ni, Cr, or Ti, or an alloy of metals appropriately selected from these. The reflection layer 7 is provided with a view to attaining a heat radiating effect or an optical effect such as an effective light absorption at the recording layer 4. When, for instance, a layer configuration is capable of sufficient heat radiation, however, the reflection layer 7 is not indispensable. In the case where the reflection layer 7 is provided, it preferably has a thickness of not less than 1 nm. Otherwise, namely, when the thickness is less than 1 nm, the reflection layer 7 hardly can be formed in a film form with a uniform thickness, thereby impairing the thermal and optical effects.

[0036]

The following description will depict the recording layer 4. The recording layer 4 contains, as a main component, a semiconductor or a half metal that can exhibit a reversible transition between a crystalline state and an amorphous state in response to an energy beam such as the laser beam irradiating the same. An energy gap of the semiconductor or the half metal (an optical gap energy)  $E_0$  in the case where the recording layer 4 is in the amorphous state is not less than 0.9 eV and not more than 2.0 eV.

[0037]

The following description will depict a method for determining an optical gap energy. An absorption spectrum in the vicinity of a fundamental absorption edge of an amorphous semiconductor is described approximately by the formula (1) below that is known as a Tauc plot (see, for instance, "Amorphous Semiconductor" published by Baifukan, page 38, Formula (3.8)):

[0038]



$$\alpha(E) \cdot E \propto (E - E_0)^2 \quad \dots (1)$$

where  $\alpha(E)$  represents an absorption coefficient,  $E$  represents an energy of light, and  $E_0$  represents an optical gap energy.

[0039]

Here, considering  $\alpha(E) \propto ka(E) \cdot E$  (where  $ka(E)$  represents an extinction coefficient of the material with respect to light with an energy  $E$ ), the following formula (2) is derived:

$$(ka(E))^{1/2} \cdot E \propto E - E_0 \quad \dots (2)$$

According to the formula (2), when the energy  $E$  of light is varied (in other words, the wavelength of the light is varied), the value of  $(ka(E))^{1/2} \cdot E$  and the value of  $E$  have a linear relationship therebetween, as is expressed by a straight line in a plane formed by an x axis indicating the value of  $E$  and a y axis indicating the value of  $(ka(E))^{1/2} \cdot E$ . Here, an X-axis segment of this straight line indicates an optical gap energy  $E_0$ .

[0040]

FIG. 2 shows  $E_0$  in the case of  $Sb_2Se_3$  as an example of a recording layer material. Measurement of  $ka(E)$  was carried out by ellipsometry using a sample with a thickness of 10 nm. According to the graph,  $E_0$  of  $Sb_2Se_3$  in the amorphous state was found to be 1.39 eV.  $E_0$  of  $Sb_2Se_3$  in the crystalline state was found to be 1.16 eV. For comparison,  $E_0$  of  $Ge_2Sb_2Te_5$ , which is known as a material having excellent characteristics in the red wavelength range, was determined in the same manner. As a result, the value of  $E_0$  of  $Ge_2Sb_2Te_5$  was found to be 0.73 eV in the amorphous state, and 0.35 eV in the crystalline state.

[0041]

It should be noted that the recording layer preferably is configured so that substantially the entirety of the same is made of a material having an energy gap ranging 0.9 eV to 2.0 eV when it is in the amorphous state. As long as the object of the present invention is achieved, however, another minor component may be contained therein at a rate not exceeding 50 at%, preferably not exceeding 10 at%.

[0042]

The following description will depict the relationship between the value of  $E_0$  of the recording layer and the optical characteristics of the optical information recording medium.

FIGS. 3(a) and 3(b) illustrate the outcomes of measurement

regarding the wavelength-dependent refractive index and the wavelength-dependent extinction coefficient of  $\text{Sb}_2\text{Se}_3$ , respectively. FIGS. 4(a) and 4(b) illustrate the outcomes of measurement regarding the wavelength-dependent refractive index and the wavelength-dependent extinction coefficient of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , respectively. Here, the refractive index is equivalent to the real part of the complex refractive index, and the extinction coefficient is equivalent to the imaginary part of the complex refractive index.

[0043]

Comparing FIG. 3(b) and FIG. 4(b), it can be seen that peaks of the extinction coefficient of  $\text{Sb}_2\text{Se}_3$  both in the amorphous state and in the crystalline state shift to the short wavelength side, as compared with those of the  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ . For instance,  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  in the amorphous state has an extinction coefficient of not more than 2.0 when the wavelength is in a range of not less than 600 nm, while  $\text{Sb}_2\text{Se}_3$  has an extinction coefficient at the same level when the wavelength is in a range of not less than 350 nm. Further, comparing FIG. 3(a) and FIG. 4(a),  $\text{Ge}_2\text{Sb}_2\text{Te}_5$  both in the amorphous state and in the crystalline state exhibits a decrease in the refractive index on the short wavelength side, while  $\text{Sb}_2\text{Se}_3$  exhibits such a decrease in the refractive index further on the short wavelength side. Thus,  $\text{Sb}_2\text{Se}_3$  exhibits optical characteristics that shift to the short wavelength side, as compared with  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ . This is because the value of the optical gap energy of  $\text{Sb}_2\text{Se}_3$  is high relative to that of  $\text{Ge}_2\text{Sb}_2\text{Te}_5$ , and hence it has an absorption edge further on the short wavelength side.

[0044]

Generally, extinction coefficients of an amorphous material and a semiconductor material with respect to a wavelength in the vicinity of absorption edges gradually increase as the wavelength decreases. In the case where a material with a relatively greater optical gap energy is used, the absorption edge shifts to the high energy side (short wavelength side), and therefore, the increase in the extinction coefficient takes place further on the short wavelength side. The utilization of this principle allows absorption of light with a certain specific wavelength in the recording layer to be adjusted optimally by adjusting the optical gap energy of the recording material. The inventors of the present invention focused on this principle, and determined values of optical gap energy of various phase-change

materials, and measured optical constants of these materials. As a result, they discovered that, as to the so-called blue wavelength range, when a material was used that had an optical gap energy  $E_0$  of not less than 0.9 eV and not more than 2.0 eV in the amorphous state, an optimal extinction coefficient was obtained, whereby light absorption was optimized easily.

[0045]

In the case where the recording layer is in the crystalline state, it seems difficult to determine the optimal range of the optical gap energy. This is because in some cases the phase change from the amorphous state to the crystalline state leads to, not only the absorption edge shift, but also transition from a semiconductor to a half metal. For instance, FIG. 5 shows a graph for determining an optical gap energy of  $\text{Ge}_4\text{Sb}_2\text{Te}_7$ . According to FIG. 5,  $E_0$  in the amorphous state is found to be approximately 0.73 eV, but by the same method,  $E_0$  in the crystalline state cannot be found to be a positive value. A tilt of the straight line in FIG. 5 in the amorphous state significantly differs from that in the crystalline state. This is because the phase change from the amorphous state to the crystalline state involves, not only the absorption edge shift, but also transition from the semiconductor state to the half metal state. In such a case as this, however, excellent optical characteristics are obtained with respect to the blue wavelength range as long as the value of  $E_0$  in the amorphous state is in the foregoing range. Generally, a material that exhibits the phase change as shown in FIG. 5 is rather preferable, since the phase change tends to involve an increased change in the optical characteristics, rather than the absorption edge shift.

[0046]

Incidentally, as shown in FIG. 2, in the case of a material whose  $E_0$  in the crystalline state is found to be a positive value, the material preferably satisfies  $E_0(c) \leq E_0(a) - 0.15$ , where  $E_0(c)$  represents an optical gap energy in the crystalline state, and  $E_0(a)$  represents an optical gap energy in the amorphous state. When this condition is satisfied, this means that the optical characteristics in the crystalline state and those in the amorphous state differ sufficiently from each other, and hence, it is possible to obtain a high C/N ratio readily.

[0047]

In the case where a material whose optical gap energy  $E_0$  in the

amorphous state is less than 0.9 eV is used for forming the recording layer, an excessively great extinction coefficient is obtained with respect to the blue wavelength range from 350 nm to 450 nm. This leads to an increase in light absorption in a recording layer with respect to the laser beam. Therefore, with this material, it particularly is difficult to form an information layer with a high transmittance. Besides, since empirically the refractive index often decreases as the extinction coefficient increases, the use of the foregoing material often makes it difficult to obtain a high C/N ratio and a high reflectance as a medium.

[0048]

On the other hand, in the case where a material whose  $E_0$  is more than 2.0 eV is used for forming the recording layer, the absorption edge excessively shifts to the short wavelength side, thereby causing the extinction coefficient to be excessively small in the blue wavelength range. In this case, the thickness of the recording layer 4 is required to be increased to at least 50 nm, since otherwise the recording sensitivity lowers. Such an increase in the thickness of the recording layer 4, however, leads to problems such as adjacent mark erasure due to in-plane heat diffusion in the recording layer, and an increase in a heat capacity that causes a cooling speed to lower, thereby disabling the formation of sufficient-size recording marks (amorphous marks), and hence, lowering the C/N ratio. Furthermore, generally a material having an excessively great  $E_0$  tends to have a small refractive index, and hence tends to cause inconveniences such as insufficient C/N ratio and an insufficient reflectance.

[0049]

For the foregoing reasons, a material with  $E_0$  in the amorphous state ranging from 0.9 eV to 2.0 eV is used for forming the recording layer 4.  $E_0$  preferably is not less than 1.0 eV, and more preferably not less than 1.5 eV.

[0050]

The material of the recording layer 4, as described above, preferably satisfies  $n_a > 2.5$ ,  $n_c > 2.5$ , and  $k_a < 2.0$ , with respect to wavelengths in the laser beam wavelength range, more specifically throughout the wavelength range from 350 nm to 450 nm. When  $n_c$  or  $n_a$  is not more than 2.5, a light absorptance of the recording layer decreases, thereby likely causing inconveniences, such as lowered recording sensitivity and insufficient reflectance. Further, when  $k_a$  is not less than 2.0, light absorption at the

recording layer 4 excessively increases, thereby making it difficult to form an information layer of the light transmission type. Incidentally, a material satisfying the foregoing conditions exhibits an excellent property with respect to the wavelengths ranging from 300 nm to 350 nm, as compared with the material for red wavelength range use.

[0051]

Furthermore,  $k_c$  and  $k_a$  more preferably satisfy the relationship  $|k_c - k_a| \geq 0.5$ . A difference between the optical characteristics increases as the difference between the extinction coefficients increases, thereby allowing a higher C/N ratio to be obtained. Further,  $n_a$  and  $n_c$  more preferably satisfy the relationship expressed as  $n_a - n_c \leq 1.0$ . This is because when  $n_c$  is great relative to  $n_a$ , it is easier to design the recording layer 4 so that a light absorptance  $A_c$  of the recording layer 4 in the crystalline state is greater than a light absorptance  $A_a$  of the recording layer 4 in the amorphous state. As will be described later in detail, when  $A_c > A_a$ , it is possible to compensate a difference between a temperature rise in a crystalline part and a temperature rise in an amorphous part in the recording layer 4, which is caused by the latent heat of crystallization, thereby allowing the heat balance to be maintained. This makes it possible to reduce mark deformation that takes place upon overwrite recording.

[0052]

The recording layer 4 preferably is made of a material that has a high crystallization kinetic, and exhibits high stability in the amorphous state. For this purpose, it is necessary to select a recording layer material appropriately, regarding its composition, crystalline structure, temperature of crystallization, melting point, etc. Generally, when the crystalline structure is a NaCl-type fcc structure, it is likely to obtain a high crystallization kinetic. This seems to be because, in the case of the NaCl type, only small atom migration takes place upon the phase change from the amorphous state to the crystalline state, thereby allowing the crystallization kinetic to increase generally. The mechanism of crystallization process, however, is not simple, and all factors determining the crystallization kinetic have not been discovered completely.

[0053]

A material is more crystallizable if it has a low crystallization temperature, whereas the stability of the material in the amorphous state

deteriorates if the crystallization temperature is excessively low. Generally, a material having a crystallization temperature in a range of 150°C to 250°C is preferable. Further, since the use of a material having an excessively high melting point causes the recording sensitivity to lower, it is preferable to select an optimal value as to the melting point (for instance, around 500°C to 750°C).

[0054]

Specific examples of materials forming the recording layer 4 include phase-changeable materials containing Se as a main component. They are materials containing as main components, for instance, Sb-Se, Sn-Se, Se-Ge, Se-Si, In-Se, Ga-Se, Al-Se, and Bi-Se, respectively. A material containing Se as a main component generally has a great optical gap energy, as compared with a material containing Te as a main component, and many of the foregoing materials satisfy the condition that the optical gap energy is between 0.9 eV and 2.0 eV. When a content of Se is lower than 20 at%, it is slightly difficult to get an optical gap energy of not less than 0.90 eV. Therefore, the content of Se preferably is not less than 20%.

[0055]

As the material for forming the recording layer 4, preferable is a material that contains the above-exemplified binary Se compound as a main component, and further, some additives. As to the additive, it is preferable that a third material is added alone, or that third and fourth materials are added in combination.

[0056]

The third material is added mainly with a view to adjustment of the crystallization kinetic and expansion of differences between optical characteristics in the amorphous state and those in the crystalline state. Examples of the third material include Al, Ga, In, Si, Ge, Sn, Sb, Bi, Sc, Ti, Nb, Cr, Mo, Co, and appropriate mixtures of any of these. Ge, In, Sn, and Bi are preferable in particular. The third material preferably is selected from the group consisting of materials other than the binary components contained as the main component.

[0057]

The fourth material is added for the purpose of improving the repetitive recording characteristics, preventing oxidation of the recording layer 4, and the like. Preferably applicable as the fourth material are Cu,

Ag, Au, Pd, Pt, N, O, Cr, Al, Si, and appropriate mixtures of any of these. By adding such a material, the material flow of the recording layer 4 upon repetitive recording is suppressed, whereby the repetitive recording characteristics can be enhanced. By adding a material that is oxidized easily and whose oxide exhibits poor solubility in water, for instance, Cr, Al, or Si, corrosion resistance and oxidation resistance of the recording layer 4 are improved drastically.

[0058]

The following description will depict a preferable process for determining a composition ratio of the recording layer 4. First of all, as to the binary material as a base, a composition ratio of Se and an element other than Se is varied so that an optimal composition is selected with which both a high crystallization kinetic and a high stability in the amorphous state are obtained. Then, the third material is added thereto, whose added quantity is varied, so that an optimal added quantity is determined with which a maximum difference between optical characteristics in the amorphous state and in the crystalline state, and both high crystallization kinetic and a high stability in the amorphous state are obtained. Furthermore, to the trinary material thus determined, the fourth material is added while a quantity of the same is varied, so that an added quantity that provides most excellent repetitive recording characteristics and corrosion resistance is determined.

[0059]

Specific examples of preferable materials containing Se include Se-In-Ge, Se-Sb-Ge, Se-Sn-In, Se-Sn-Al, Se-Bi-Ge, Se-In-Ge-N, and Se-Bi-Al-N.

[0060]

Other examples of materials for forming the recording layer include phase-change materials containing Te as a main component. The materials containing Te as a main component generally have an optical gap energy that is small relative to that of the material containing Se, but some of the same satisfy the condition that the optical gap energy is not less than 0.9 eV. They are, for instance,  $\text{In}_2\text{Te}_3$ ,  $\text{InTe}$ ,  $\text{Ga}_2\text{Te}_3$ ,  $\text{GaTe}$ ,  $\text{Al}_2\text{Te}_3$ ,  $\text{ZnTe}$ , and  $\text{MnTe}$ .

[0061]

In the case where a recording layer containing Te is used, the

aforementioned element X may be added as well, whereby the optical gap energy relatively easily can be adjusted so as to be in the foregoing range. The composition ratio thereof preferably is such that Te accounts for between 20 at% and 60 at% while the element X accounts for between 20 at% and 50 at%. By so doing, a material is prepared readily that exhibits sufficiently high stability in the amorphous state and has a high crystallization kinetic.

[0062]

The material of the recording layer 4 preferably contains Te and the element X as the main component, and further includes the foregoing third and/or fourth materials as additives. Preferable materials as the third and fourth materials are the same as above. The composition ratio may be determined in the same manner as described above.

[0063]

Specifically, examples of preferable materials containing Te include Te-In-Ge, Te-In-Sb, Te-In-Si, Te-Ga-Sb, Te-Al-Sb, Te-Al-Bi, Te-Al-Ge-N, and Te-Mn-Sb-In.

[0064]

Still other examples of the material for forming the recording layer include materials containing Sb as the main component. In this case, Al-Sb, Ga-Sb, Sb-S, Sb-Se, or the like preferably is contained as the main component. These materials also can be made to have excellent phase change characteristics by adding the foregoing third and/or fourth materials. Specific examples of such a material include Sb-Al-Ge, Sb-Al-In, Sb-Al-Ga, Sb-Sn-Al, Sb-Sn-Al-N, and Sb-In-Ge-N.

[0065]

It should be noted that the recording layer may contain impurities such as Ar or Kr as a sputtering gas component, H, C, or H<sub>2</sub>O, whose existence is tolerable as long as their content is controlled to a level such as not to affect recording/reproduction of signals. Furthermore, in some cases, a very small amount (approximately not more than 10 at%) of another substance may be added to the main components for various purposes other than those described above. In such a case also, the content of the same preferably is controlled to a level such as not to affect recording/reproduction of signals.

[0066]



The recording layer preferably has a thickness ranging from 1 nm to 25 nm. If the thickness thereof is set less than 1 nm, it is difficult to obtain a layer of the recording material with a uniform thickness, and it is difficult to cause a change in the state that leads to a change in the optical characteristics. On the other hand, if the thickness thereof is set more than 25 nm, in-plane heat diffusion in the recording layer increases, thereby resulting in that adjacent mark erasure tends to occur upon high-density recording.

[0067]

A light absorptance  $A_c$  of the recording layer in the crystalline state preferably is greater than a light absorptance  $A_a$  of the recording layer in the amorphous state. In the case of the phase-change recording material, recording marks are formed at different positions before and after information rewriting, respectively, and therefore, it is necessary to simultaneously carry out, upon rewriting, four types of phase changes, that is, "from the crystalline state to the crystalline state", "from the crystalline state to the amorphous state", "from the amorphous state to the crystalline state" and "from the amorphous state to the amorphous state". Here, the change from the crystalline state to the amorphous state requires a great amount of heat relative to an amount of heat required for the change from the amorphous state to the amorphous state, since the former change needs latent heat for melting. Therefore, when  $A_c \leq A_a$ , an extra amount of heat is generated at a portion where a change from the amorphous state to the amorphous state takes place, thereby causing unbalanced temperature rises in the amorphous portions and the crystalline portions. This tends to cause deformation of recording marks. However, when  $A_c > A_a$ , temperature rises are well-balanced, whereby deformation of overwritten recording marks is unlikely to occur. This makes it possible to obtain excellent-quality signals. For the foregoing reason, the thicknesses of layers preferably are set so as to satisfy  $A_c > A_a$ .

[0068]

The following description will depict a method for producing an optical information recording medium. Applicable as methods for forming a multi-layer film constituting an optical information recording medium are sputtering, vacuum deposition, CVD, etc. Here, as an example, a method for forming a multi-layer film by sputtering is described. FIG. 6 shows a

schematic configuration of an example of a film forming device by sputtering. In this device, a vacuum pump (not shown) is connected to a vacuum chamber 8 via an air outlet 14 so that a high vacuum is maintained in the vacuum chamber 8. A gas supply port 13 allows rare gas, nitrogen gas, oxygen gas, or a mixture of these gases to be introduced at a certain set flow rate. The device also is provided with a driving device 10 for planetary motion of the substrate 9. Sputtering targets 11 are connected with cathodes 12, respectively. The cathodes 12 are connected to a direct current power source or a high frequency power source via switches, though not shown in the drawing. By grounding the vacuum chamber 8, the vacuum chamber 8 and the substrate 9 are maintained to be anodes. Used as a film forming gas is a rare gas, or a rare gas to which a very small quantity of nitrogen and oxygen is added. Ar, Kr or the like may be used as the rare gas.

[0069]

To form the recording layer 4 and the protective layers 2 and 6, a gas mixture composed of a rare gas and a very small quantity of nitrogen or oxygen preferably is used. This allows mass transfer upon repetitive recording of the medium to be suppressed, thereby resulting in improvement of the repetitive recording characteristics.

[0070]

Furthermore, in the case where a nitride, oxide, or oxynitride is used as the main component constituting the interface layers 3 and 5, a film with excellent quality is obtained by reactive sputtering. For instance, in the case where Ge-Cr-N is used for forming the interface layers, a material containing Ge and Cr and a gas mixture composed of a rare gas and nitrogen may be used as the target and as the film forming gas, respectively. Alternatively, a gas mixture composed of a rare gas and a gas whose molecule contains at least one nitrogen atom, such as  $N_2O$ ,  $NO_2$ ,  $NO$ , or  $N_2$  may be used.

[0071]

The following description will explain a method for recording/reproducing on/from an optical information recording medium. FIG. 7 shows, as one example, a schematic configuration of a device used for recording/reproduction. For recording, reproduction and erasure of signals, this device is provided with a laser beam source 15, an optical head on

which an objective lens 16 is mounted, a driving device 18 for guiding a portion to be irradiated with the laser beam to a predetermined position, a tracking control device and a focusing control device (not shown) for controlling the position in the tracking direction and the perpendicular direction to the film surface, a laser driving device (not shown) for modulating a laser power, and a rotation control device 19 for rotating the optical information recording medium (optical disk 17).

[0072]

Recording and erasure of signals are carried out by rotating the optical disk 17 by means of the rotation control device 19 and by irradiating the medium with the laser beam converged to a microspot by means of the optical system. An amorphous-state-producing power level of the laser beam that causes only a portion of the recording layer irradiated with the laser beam to reversibly change to the amorphous state is given as P1, while a crystalline-state-producing power level thereof that causes an irradiated portion to reversibly change to the crystalline state is given as P2. By modulating the laser power between P1 and P2, recording marks are formed or erased, so that information is recorded, erased, or overwritten. Irradiation with the laser beam having the power level P1 preferably is carried out according to a pulse string, that is, a so-called multiple pulse.

[0073]

Furthermore, a power level that is lower than both of P1 and P2, laser irradiation which does not affect an optical state of a recording mark but allows a sufficient reflectance to be obtained for reproduction of recording marks from the medium is given as a reproduction power level P3, and signals from the medium that are obtained by irradiation with the laser beam having the power level P3 are read by a detector (not shown), so that an information signal is reproduced.

[0074]

A wavelength of the laser beam used for recording/reproduction preferably is not more than 450 nm, for instance, in a range of 300 nm to 450 nm, particularly in a range of 350 nm to 450 nm. This is intended to cause an effect of the medium of the present invention to be exhibited fully, thereby allowing high-density recording. Incidentally, the laser wavelength for recording signals and the laser wavelength for reproduction are not necessarily the same. Furthermore, in the case of a multi-layer recording

medium for which recording/reproduction can be carried out from one side, laser wavelengths for recording/reproduction of the respective media may be all the same, or may be partly different.

[0075]

An optical information recording medium of the present invention preferably is configured so as to be a so-called multi-layer recording medium. Further, the recording medium could be configured so that recording/reproduction to/from a plurality of information layers is conducted by laser irradiation from only one side, whereby higher-density recording is ensured.

[0076]

FIG. 8 illustrates an example of a configuration of a light-transmission-type multi-layer recording medium. In this medium,  $n$  sets of information layers ( $n$  is a natural number satisfying  $n \geq 2$ ) are laminated on a substrate 35, with separating layers 37, 39, ... and 41 interposed therebetween. In this case, the information layers except the  $n$ 'th information layer 42, that is, the information layers from the laser incident side to the  $(n-1)$ th information layer (from a first information layer 36, a second information layer 38, to the  $(n-1)$ th information layer 40), preferably are configured so as to be light-transmission-type information layers. The light-transmission-type information layer is configured so that the transmittance of the laser beam is not less than 30%. In this case, it is possible to carry out recording/reproducing to the  $k$ 'th medium ( $k$  is a natural number satisfying  $1 < k \leq n$ ) only by laser irradiation from one side, beyond the first through  $(k-1)$ th media. However, a configuration satisfying  $n = 2$ , that is, having two information layers, is practical.

[0077]

The separating layers 37, 39, ..., and 41 preferably are transparent layers, and can be made of a resin such as a UV-hardening-type resin or a slow-acting resin, or a dielectric.

[0078]

It should be noted that, as the  $n$ 'th information layer 42, a recording layer made of a conventional recording material that is optimized for the red wavelength range may be adapted, but it is more advantageous for optical designing to adapt an information layer characterized according to the present invention. Furthermore, any one of the information layers may be

configured so as to be a read-only information layer (read only memory (ROM)), or a write-once information layer.

[0079]

The following description depicts the multi-layer recording medium in more detail, by taking a case where  $n = 2$  as an example.

FIG. 9 is a cross-sectional view of one embodiment of a multi-layer recording medium having two sets of media. In this embodiment, a first information layer 110 is composed of a first protective layer 102, a first interface layer 103, a recording layer 104, a second interface layer 105, a second protective layer 106, and a reflection layer 107 that are laminated in the stated order from the side of a substrate 101, and likewise, a second information layer 210 is composed of a first protective layer 202, a first interface layer 203, a recording layer 204, a second interface layer 205, a second protective layer 206, and a reflection layer 207 that are laminated in the stated order from the side of the substrate 101. Between the information layers 110 and 210, a separating layer 108 is provided, which is intended mainly to optically separate these information layers.

[0080]

The separating layer 108 is made of a material that exhibits as small a light absorption as possible to the laser beam. More specifically, a resin made of an organic material such as a UV-hardening resin or a slow-acting resin, an optical-disk-use double-sided adhesive sheet, an inorganic dielectric such as  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , or  $\text{ZnS}$ , a glass material, etc. are applicable preferably. It is necessary to cause the separating layer 108 to have a thickness of not less than twice a depth of focus  $\Delta Z$  of the laser beam so that upon recording/reproduction of one of the media, crosstalk from the other medium is suppressed to an ignorable level. Here, the depth of focus  $\Delta Z$  from a reference point at which light intensity is 80% of the light intensity at the focal point in the case of non aberration is expressed approximately by a formula (3) below:

[0081]

$$\Delta Z = \lambda / \{2 \times (\text{NA})^2\} \quad \dots (3)$$

Here, NA represents a numerical aperture of the objective lens, and  $\lambda$  represents a wavelength of the laser light upon recording/reproduction. For instance when  $\lambda = 400 \text{ nm}$  and  $\text{NA} = 0.60$ , the depth of focus  $\Delta Z$  is  $0.56 \text{ }\mu\text{m}$ . In other words, since a range of approximately  $\pm 0.60 \text{ }\mu\text{m}$  is included in

the depth of focus, the separating layer 108 preferably has a thickness of more than 1.20  $\mu\text{m}$ . Incidentally, the thickness of the separating layer 108 preferably is in a range of a permissible tolerance of the objective lens, so that a distance between two information layers falls in a range in which the objective lens is able to converge light.

[0082]

To the second information layer 210, information is recorded/reproduced by the laser beam that has passed through the first information layer 110. Therefore, when  $T_1$  and  $R_1$  respectively represent a transmittance and a reflectance of the first information layer with respect to the laser beam for recording/reproduction and  $R_2$  represents a reflectance of the second information layer, a reflectance  $r_2$  upon reproduction of the second information layer beyond the first information layer is expressed by a formula (4) below:

[0083]

$$r_2 = R_2 \times T_1 \times T_1 \quad \dots (4)$$

[0084]

Furthermore, as to a signal amplitude, when  $\Delta R_2$  represents a differential reflectance of the second information layer per se and  $\Delta r_2$  represents a differential reflectance of the second information layer when being reproduced beyond the first information layer, the relationship expressed by a formula (5) below is satisfied:

[0085]

$$\Delta r_2 = \Delta R_2 \times T_1 \times T_1 \quad \dots (5)$$

[0086]

For instance, when  $\Delta R_2 = 24\%$  and  $T_1 = 50\%$ , the differential reflectance  $\Delta r_2$  upon reproduction of the second information layer beyond the first information layer is obtained as  $\Delta r_2 = 24\% \times 0.5 \times 0.5 = 6\%$ . To obtain sufficient signals from the second information layer, it is preferable that the transmittance of the first information layer is set as high as possible, while the signal amplitude of the second information layer is set as great as possible. Simultaneously, it is preferable that the differential reflectance of the first information layer is set to a certain high level, while the recording sensitivity of the second information layer is set high. The optical design of the first and second information layers is determined so that these factors are all well-balanced.

[0087]

The following description will depict a specific example of the optical design. As one example, the first and second information layers are optically designed so that the first information layer has a reflectance  $R1c$  of 7.5% when the recording layer 104 is in the crystalline state and a reflectance  $R1a$  of 0.5% when it is in the amorphous state, the second information layer 210 has a reflectance  $R2c$  of 15% when the recording layer 204 is in the crystalline state and has a reflectance  $R2a$  of 43% when it is in the amorphous state. Furthermore, the transmittance of the first information layer when recording is conducted only on the first information layer is set to 50%. The foregoing optical characteristics are adjusted by varying the respective thicknesses of the recording layer 104, the protective layers 102 and 106 and the reflective layer 106.

[0088]

In the foregoing example, the differential reflectance when the recording/reproduction on/from the second information layer 210 is carried out beyond the first information layer 110 was obtained as  $(43 - 15) \times 0.5 \times 0.5 = 7\%$ , and the differential reflectance of the first information layer 110 was obtained as  $7.5 - 0.5 = 7\%$ . Thus, it is preferable that differential reflectances, that is, signal amplitudes, of the first and second information layers are set substantially equal. This is because the tracking is unstabilized if the signal amplitude extremely varies when a target of recording/reproduction is shifted from an information layer to another.

[0089]

Since it is very difficult to obtain compatibly a high transmittance of the first information layer and a high differential reflectance of the second information layer, the differential reflectance as a result of designing is relatively small, and hence the signal amplitude is relatively small. In this case, it is preferable that the power level  $P3$  of the light beam for reproduction is set relatively higher than conventionally so that a great reproduction signal amplitude is obtained. If the level of  $P3$  is set excessively high, however, recording marks are thermally affected, resulting in deterioration of the reproduction signals. Therefore, the reproduction power level of  $P3$  preferably is set in a range such that it does not cause the signal deterioration. Incidentally, the reproduction power levels for the first information layer and the second information layer may differ from

each other. Besides, the wavelengths of the laser beams for reproduction of the information layers may differ from each other, but ordinarily laser beams with the same wavelength are used.

[0090]

The light transmittance of the first information layer when information is reproduced from the second information layer preferably is not less than 30%, more preferably not less than 50%. The signal amplitude upon recording/reproduction of information on/from the second information layer beyond the first information layer has a value multiplied by a square of the transmittance of the first information layer. Therefore, if the light transmittance of the first information layer is smaller than 30%, the signal amplitude has a value multiplied by 0.09 or less, which is considerably small. Therefore, to bring the signal amplitudes of both the information layers into balance, the light transmittance of the first information layer has to be set to a certain high level. Besides, if the transmittance of the first information layer is set very low, for instance less than 30%, a quantity of light reaching the second information layer significantly decreases, thereby causing the recording sensitivity of the second information layer to deteriorate.

[0091]

Furthermore, the reflectance  $R_{1c}$  with respect to the laser beam when the recording layer 104 of the first information layer is in the crystalline state preferably is higher than the reflectance  $R_{1a}$  when the recording layer 104 is in the amorphous state. This is because  $R_c$  has to be higher than a certain value (for instance, about 5% to 10%) in order to enable stable tracking, and when the medium is optically designed so as to satisfy  $R_a > R_c > \alpha$  ( $\alpha$  is a constant positive number), the transmittance and the absorptance of the medium decrease for the foregoing  $\alpha$ , which is a disadvantage from the viewpoint of the optical design.

[0092]

[Examples]

The present invention will be explained in detail by way of examples below, but is not limited thereto.

[0093]

(Example 1)

The same configuration as that shown in FIG. 9 was further



configured so that: the substrate 101 was made of a polycarbonate resin in a disk form with a thickness of 0.6 mm and a diameter of 120 mm; protective layers 102, 106, 202, and 206 all were made of ZnS containing 20 mol% of SiO<sub>2</sub>; the interface layers 103, 105, 203, and 205 all were made of GeCrN; the reflection layer 107 was made of an AgPdCu alloy; the reflection layer 207 was made of an AgPdTi alloy; the recording layer 104 was made of Ge<sub>20</sub>In<sub>45</sub>Se<sub>30</sub>Cr<sub>5</sub>; and the recording layer 204 was made of Ge<sub>4</sub>Sb<sub>2</sub>Te<sub>7</sub>. The thicknesses of these layers were set as follows: the recording layers 104 and 204 were 7 nm and 9 nm in thickness, respectively; the interface layers 103, 105, 203, and 205 were 2 nm in each thickness; the reflection layers 107 and 207 were 5 nm and 60 nm in thickness, respectively; the protective layers 102 and 106 were 65 nm and 45 nm in thickness, respectively; and the protective layers 202 and 206 were 90 nm and 40 nm, respectively.

[0094]

Incidentally, in setting the thicknesses of the protective layers 102 and 106, optical characteristics that the medium had when the respective thicknesses were varied from 0 to  $\lambda/2n$  ( $\lambda$  represents a wavelength of the laser beam and  $n$  represents a refractive index of the material of the protective layer with respect to the wavelength  $\lambda$ ) were considered. According to this, the thicknesses of the protective layers 102 and 106 were selected that provide a high transmittance and a high differential reflectance of the first information layer. Furthermore, a substrate on which grooves and lands were formed alternately at a track pitch of 0.39  $\mu\text{m}$  was adapted as the substrate 101.

[0095]

Here, for forming the recording layers 104 and 204, Ar gas containing 2.5 % of nitrogen was supplied so that a total pressure of 0.13 Pa was obtained, and a DC power of 1.27 W/cm<sup>2</sup> was fed to the cathodes. For forming the protective layers 102, 106, 202 and 206, Ar gas containing 1.0% of oxygen was supplied so that a total pressure of 0.13 Pa was obtained, and a RF power of 5.10 W/cm<sup>2</sup> was supplied to the cathodes. For forming the reflection layers 107 and 207, Ar gas was supplied so that a total pressure of 0.26 Pa was obtained, and a DC power of 4.45 W/cm<sup>2</sup> was supplied. For forming the interface layers 103, 105, 203, and 205, a target material was GeCr, a sputtering gas was a gas mixture of Ar and nitrogen (partial pressure of nitrogen: 30%), a sputtering gas pressure was set to 1.33 Pa, and

a RF sputtering power density was set to 6.37 W/cm<sup>2</sup>.

[0096]

Characteristics of the disk were evaluated according to the results of measurement of the transmittance of the first information layer, and C/N ratios and overwrite erasure rates of both the first and second information layers. The (8-16) modulation system was adapted as the signaling system for recording, and a laser beam with a wavelength of 400 nm and an objective lens with a numerical aperture of 0.60 were used for both the first and second information layers. The shortest mark length was set to 0.26  $\mu$ m and the disk rotation speed was set to a linear speed of 5.0 m/s.

[0097]

The C/N ratio was evaluated in the following manner: 3T-long marks were recorded with an appropriate laser power by the (8-16) modulation system, and a C/N ratio was measured. The overwrite erasure characteristic was evaluated in the following manner: after 3T-long marks were recorded with an appropriate laser power by the (8-16) modulation system, 11T-long marks were overwritten thereon with the same power, and an erasure ratio of the 3T-long marks (hereinafter referred to as "3T erasure ratio") was measured.

[0098]

The transmittance of the first information layer was measured in the following manner: a signal amplitude in the case where a laser beam was transmitted through the first layer so as to reproduce signals in the second information layer, and a signal amplitude of the second information layer in the case where the first information layer was not formed, were measured so that a ratio between these signal amplitudes was determined. Then, based on this, a transmittance of the first information layer was calculated. More specifically, by covering a part of the disk as a medium or another method, a region where the first information layer is not present was formed in a part of the disk extending in the circumference direction, and the foregoing ratio was measured. Incidentally, the ratio was measured in a state in which information was recorded in the first information layer.

[0099]

The laser power for reproducing signals was set to 2.0 mW for both the first and second information layers. Recording/reproduction of

information on/from the second information layer was carried out in a state in which no signal was recorded in the first information layer, for the sake of convenience.

[0100]

Here, a medium in which the recording layer 104 was made of Ge<sub>20</sub>Sb<sub>30</sub>Se<sub>45</sub>In<sub>5</sub> was referred to as medium (1). For comparison, a medium that was the same as the medium (1) except that the recording layer 104 was made of Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> was referred to as medium (0), while a medium that was the same as the medium (1) except that the recording layer 104 was made of Al<sub>29</sub>Si<sub>14</sub>Se<sub>57</sub> was referred to as medium (100). The result of the evaluation of these media is shown in Table 1.

[0101]

[Table 1]

| MEDIUM NO. | RECORDING LAYER MATERIAL   | E <sub>0</sub><br>(eV) | C/N |    | ERASURE RATIO |    | TRANSMITTANCE<br>L1 |
|------------|--|------------------------|-----|----|---------------|----|---------------------|
|            |  |                        | L1  | L2 | L1            | L2 |                     |
| (1)        | Ge <sub>20</sub> Sb <sub>30</sub> Se <sub>45</sub> In <sub>5</sub> | 1.36                   | ⊙   | ⊙  | ⊙             | ⊙  | ⊙                   |
| (0)        | Ge <sub>2</sub> Sb <sub>2</sub> Te <sub>5</sub>                    | 0.73                   | ○   | ×  | ×             | ○  | ×                   |
| (100)      | Al <sub>29</sub> Si <sub>14</sub> Se <sub>57</sub>                 | 2.20                   | ×   | ○  | ×             | ×  | ⊙                   |

[0102]

Here, L1 and L2 indicate the first information layer and the second information layer, respectively. As to the C/N ratio, “⊙” indicates that the obtained C/N ratio was not less than 50 dB, “○” indicates that the obtained C/N ratio was not less than 48 dB and less than 50 dB, and “×” indicates that the obtained C/N ratio was less than 48 dB. As to the erasure characteristic, “⊙” indicates that the obtained 3T erasure ratio was not less than 35 dB, “○” indicates that the obtained 3T erasure ratio was not less than 30 dB and less than 35 dB, and “×” indicates that the obtained C/N ratio was less than 30 dB. As to the transmittance of the first information layer, “⊙” indicates that a transmittance of not less than 50% was obtained, “○” indicates that a transmittance of not less than 30% and less than 50% was obtained, and “×” indicates that a transmittance of less than 30% was obtained.

[0103]

Furthermore, Table 1 also shows values of the optical gap energy E<sub>0</sub> when the recording layer 104 was in the amorphous state, which were measured in the aforementioned manner. In this measurement, the

material of the recording layer 104 was formed in a film form with a thickness of 8 nm, and the wavelength-dependency of the optical constant was examined.

[0104]

According to Table 1, in the medium (1), both the first and second information layers had high C/N ratios and high erasure ratios. Besides, the first information layer of the same also had a sufficiently high transmittance. On the other hand, in the medium (0), when the C/N ratio of the first information layer was set not less than 48 dB, a high transmittance was not obtained, whereby the second information layer was unable to have a high C/N ratio. Besides, the erasure ratio of the first information layer thereof was insufficient. The reason for this seems to be that compensating a difference in the light absorptance between the crystalline state and the amorphous state was difficult when the C/N ratio of the first information layer was set to be high. Thus, in the case where a material has an optical gap energy of less than 0.9 eV, an extinction coefficient  $k_a$  when the recording layer 104 is in the amorphous state increases, thereby making it difficult to compatibly obtain a high transmittance and a high differential reflectance.

[0105]

Furthermore, in the case of the medium (100), the transmittance was set high easily, while it was difficult to set the C/N ratio of the first information layer to a high level. This applies even when the thicknesses of the protective layers 102 and 106 were varied. The reason for this seems to be that, since the material of the recording layer had an excessively high optical gap energy  $E_o$ , absorption of light with wavelengths of the laser beam at the recording layer decreased, thereby resulting in that the difference between optical characteristics decreased though a high transmittance was obtained. Thus, in the case where a material having an optical gap energy of not less than 2.0 eV is used, a high transmittance is obtained easily since the extinction coefficient  $k_a$  decreases sufficiently, but a signal amplitude obtained at the same time decreases excessively.

[0106]

As other examples of the present invention, media were prepared that were the same as the medium (1) except that the recording layers 104 were made of  $\text{Ge}_{18}\text{Sb}_{27}\text{Se}_{50}\text{In}_5$ ,  $\text{Ge}_{22}\text{Sb}_{33}\text{Se}_{40}\text{In}_5$ ,  $\text{Ge}_{24}\text{Sb}_{36}\text{Se}_{35}\text{In}_5$ , and

Ge<sub>26</sub>Sb<sub>39</sub>Se<sub>30</sub>In<sub>5</sub>, respectively. More specifically, the In composition ratio was maintained constant while the Se composition ratio was varied, and the contents of Ge and Sb were adjusted so that a ratio therebetween was kept constant. They are referred to as media (2) to (5), respectively. The same evaluation as described above was carried out regarding these media. The result is shown in Table 2.

[0107]

[Table 2]

| MEDIUM NO. | RECORDING LAYER MATERIAL   | E <sub>0</sub><br>(eV) | C/N |    | ERASURE RATIO |    | TRANSMITTANCE<br>L1 |
|------------|--|------------------------|-----|----|---------------|----|---------------------|
|            |  |                        | L1  | L2 | L1            | L2 |                     |
| (2)        | Ge <sub>18</sub> Sb <sub>27</sub> Se <sub>50</sub> In <sub>5</sub> | 1.40                   | ⊙   | ⊙  | ○             | ⊙  | ⊙                   |
| (3)        | Ge <sub>22</sub> Sb <sub>33</sub> Se <sub>40</sub> In <sub>5</sub> | 1.33                   | ⊙   | ⊙  | ⊙             | ⊙  | ⊙                   |
| (4)        | Ge <sub>26</sub> Sb <sub>39</sub> Se <sub>30</sub> In <sub>5</sub> | 1.28                   | ⊙   | ⊙  | ⊙             | ⊙  | ⊙                   |
| (5)        | Ge <sub>30</sub> Sb <sub>45</sub> Se <sub>20</sub> In <sub>5</sub> | 0.96                   | ○   | ⊙  | ⊙             | ⊙  | ○                   |

[0108]

Table 2 shows that both the first and second information layers had excellent characteristics in any one of the media (2) to (5). Thus, in the case where a phase-change material having an optical gap energy E<sub>0</sub> ranging from 0.90 eV to 2.0 eV is used for forming the recording layer 104, the first medium is allowed to have a high transmittance and a high C/N ratio. Therefore, both the information layers are allowed to have high C/N ratios, respectively.

[0109]

Comparing the media (1) to (5), the erasure ratio slightly decreases when the Se composition ratio in the recording layer is not less than 50 at%, while the C/N ratio slightly decreases when it is not higher than 20 at%. Therefore, the Se composition ratio particularly preferably is more than 20 at% and less than 50 at%. This preferable Se composition ratio range substantially did not change when the materials other than Se were replaced with other materials.

[0110]

When Sb and In, contained in the recording layer 104, were substituted with Sn, Ge, Si, In, Ga, Al, or Bi, substantially the same excellent characteristics were obtained. Furthermore, when Ge was substituted with a material containing at least one selected from the group consisting of Al, Ga, Si, Sn, Bi, Ti, Nb, Cr, Mo, and Co, substantially the

same characteristics were obtained.

[0111]

(Example 2)

The same media as the medium (1) except that the recording layers 104 thereof were made of Al<sub>5</sub>Ge<sub>10</sub>In<sub>15</sub>Te<sub>70</sub>, Al<sub>5</sub>Ge<sub>10</sub>In<sub>25</sub>Te<sub>60</sub>, Al<sub>5</sub>Ge<sub>10</sub>In<sub>45</sub>Te<sub>40</sub>, Al<sub>5</sub>Ge<sub>10</sub>In<sub>65</sub>Te<sub>20</sub>, and Al<sub>5</sub>Ge<sub>10</sub>In<sub>70</sub>Te<sub>15</sub>, respectively, were prepared. These media are referred to as media (6) to (10), respectively. Here, the thicknesses of films constituting the first information layer were set to the same as those of the medium (1) except that the thicknesses of the protective layers 102 and 106 were set to 90 nm and 50 nm, respectively. The second information layer had the same configuration as that of the second information layer used in the medium (1).

[0112]

The same evaluation as that for the medium (1) except that the wavelength of the recording/reproduction laser beam was set to 410 nm was carried out regarding these media (6) to (10). The result is shown in Table 3.

[0113]

[Table 3]

| MEDIUM NO. | RECORDING LAYER MATERIAL   | E0 (eV) | C/N |    | ERASURE RATIO |    | TRANSMITTANCE L1 |
|------------|--|---------|-----|----|---------------|----|------------------|
|            |  |         | L1  | L2 | L1            | L2 |                  |
| (6)        | Al <sub>5</sub> Ge <sub>10</sub> In <sub>15</sub> Te <sub>70</sub> | 0.98    | ○   | ○  | ○             | ◎  | ○                |
| (7)        | Al <sub>5</sub> Ge <sub>10</sub> In <sub>25</sub> Te <sub>60</sub> | 1.05    | ◎   | ◎  | ◎             | ◎  | ◎                |
| (8)        | Al <sub>5</sub> Ge <sub>10</sub> In <sub>45</sub> Te <sub>40</sub> | 1.10    | ◎   | ◎  | ◎             | ◎  | ◎                |
| (9)        | Al <sub>5</sub> Ge <sub>10</sub> In <sub>65</sub> Te <sub>20</sub> | 1.33    | ◎   | ◎  | ◎             | ◎  | ◎                |
| (10)       | Al <sub>5</sub> Ge <sub>10</sub> In <sub>70</sub> Te <sub>15</sub> | 1.60    | ○   | ◎  | ○             | ◎  | ◎                |

[0114]

As illustrated in Table 3, also in the present example, excellent disk characteristics were obtained as to both the first and second information layers. According to Table 3, the Te composition ratio in the recording layer preferably is not less than 20 at% and not more than 60 at%. When the Te composition ratio is set more than 60 at%, the optical gap energy tends to decrease slightly, thereby causing the transmittance of the first information layer to decrease slightly. On the other hand, when the Te composition ratio is set to less than 20 at%, the difference between the optical characteristics in the crystalline state and the amorphous state of the

recording layer 104 is slightly small, thereby causing a slightly decreased C/N ratio to be obtained. With the Te composition ratio ranging from 20 at% to 60 at%, substantially the same characteristics as described above were obtained even in the case where the materials other than Te were replaced with other materials.

[0115]

When Al, Ga, Zn or Mn is used in place of In contained in the recording layer 104, substantially the same excellent characteristics were obtained. Furthermore, when Ge is substituted with a material containing at least one selected from the group consisting of Ga, Si, Sn, Bi, Ti, Nb, Cr, Mo, and Co, substantially the same characteristics were obtained.

[0116]

[Effects of the invention]

As described above, by using a recording material having an optical gap energy ranging from 0.9 eV to 2.0 eV when the recording layer is in the amorphous state, setting a laser beam used for recording to have a wavelength ranging from 300 nm to 450 nm and setting the information layer to have a transmittance of not less than 30% with respect to this laser beam, it becomes possible to achieve an optical information recording medium including a light-transmitting-type information layer that exhibits a large transmittance even in the blue wavelength range. In this manner, it is possible to provide a multi-layer recording medium capable of high-density recording in the blue wavelength range and a recording/reproducing method thereof.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[FIG. 1] FIG. 1 is a cross-sectional view illustrating one embodiment of a layer configuration of an optical information recording medium of the present invention.

[FIG. 2] FIG. 2 is an explanatory view illustrating an example of a method for determining an energy gap of a material of a recording layer.

[FIG. 3] FIG. 3 is a view showing examples of optical constants of a material of a recording layer.

[FIG. 4] FIG. 4 is a view showing examples of optical constants of a material that conventionally is used for forming a recording layer.

[FIG. 5] FIG. 5 is a view illustrating another example of a method for determining an energy gap of a material of a recording layer.

[FIG. 6] FIG. 6 is a view illustrating an example of a film forming apparatus used for producing an optical information recording medium of the present invention.

[FIG. 7] FIG. 7 is a view illustrating an example of a device used for recording/reproduction of information to/from an optical information recording medium of the present invention.

[FIG. 8] FIG. 8 is a cross-sectional view illustrating another embodiment of a layer configuration of an optical information recording medium of the present invention.

[FIG. 9] FIG. 9 is a cross-sectional view illustrating still another embodiment of a layer configuration of an optical information recording medium of the present invention.

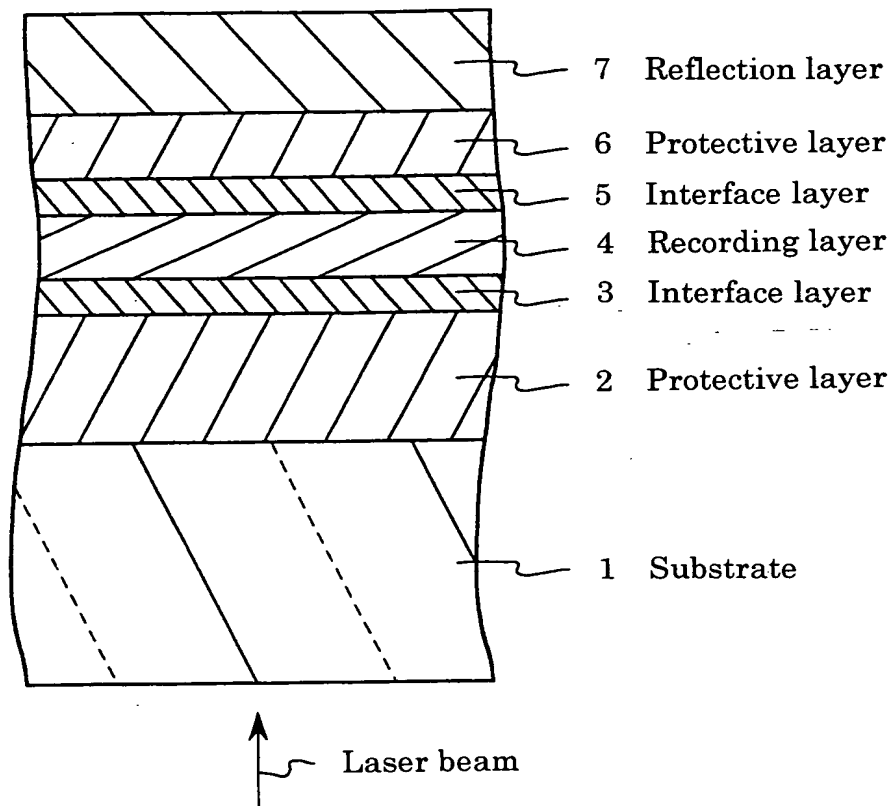
[Explanation of letters or numerals]

- 1 Substrate
- 2, 6 Protective Layer
- 3, 5 Interface Layer
- 4 Recording Layer
- 7 Reflection Layer
- 8 Vacuum Chamber
- 9 Substrate
- 10 Substrate Driving Device
- 11 Targets
- 12 Cathodes
- 13 Gas Supply Port
- 14 Air Outlet
- 15 Laser Beam Source
- 16 Objective Lens
- 17 Optical Head
- 18 Driving Device
- 19 Rotation Control Device
- 101 Substrate
- 102, 106, 202, 206 Protective Layer
- 103, 105, 203, 205 Interface Layer
- 104, 204 Recording Layer
- 107, 207 Reflection Layer
- 108 Separating Layer

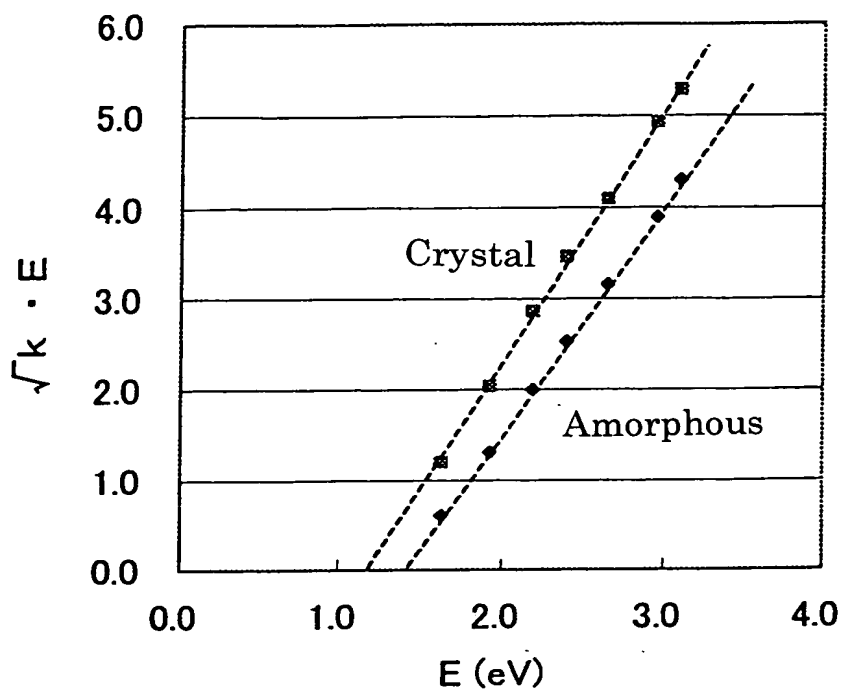


[Document Name] Drawings

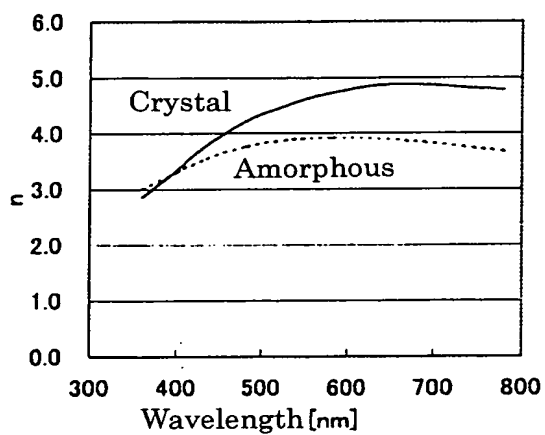
[FIG. 1]



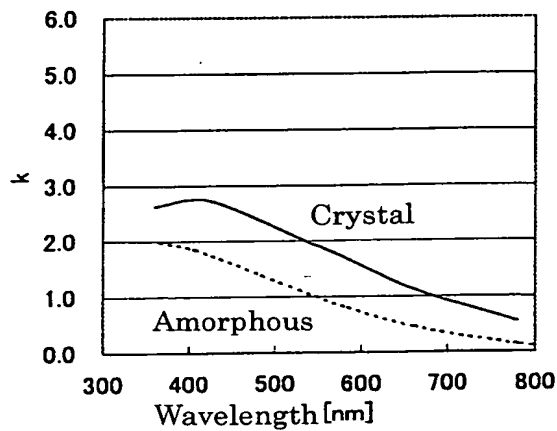
[FIG. 2]



[FIG. 3]

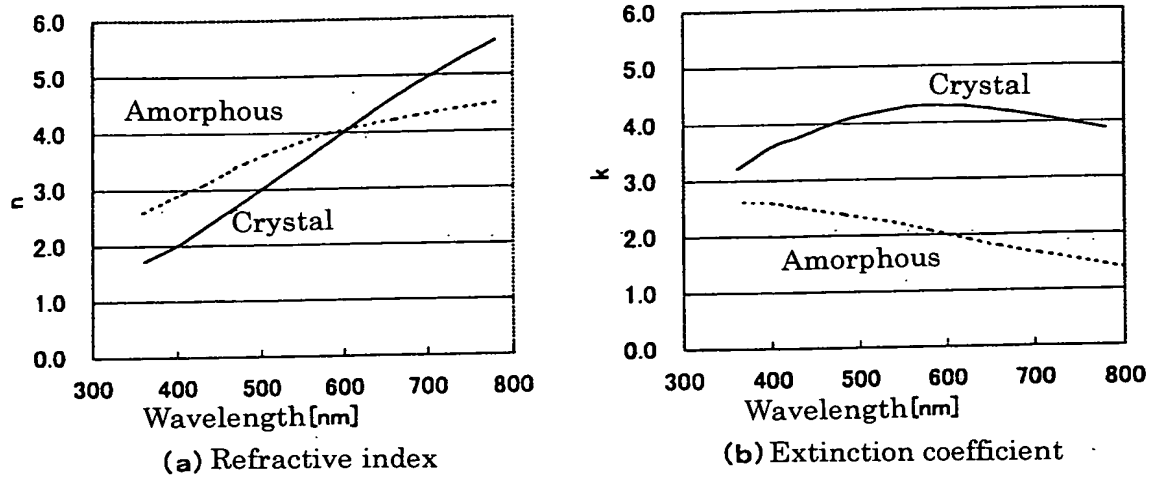


(a) Refractive index

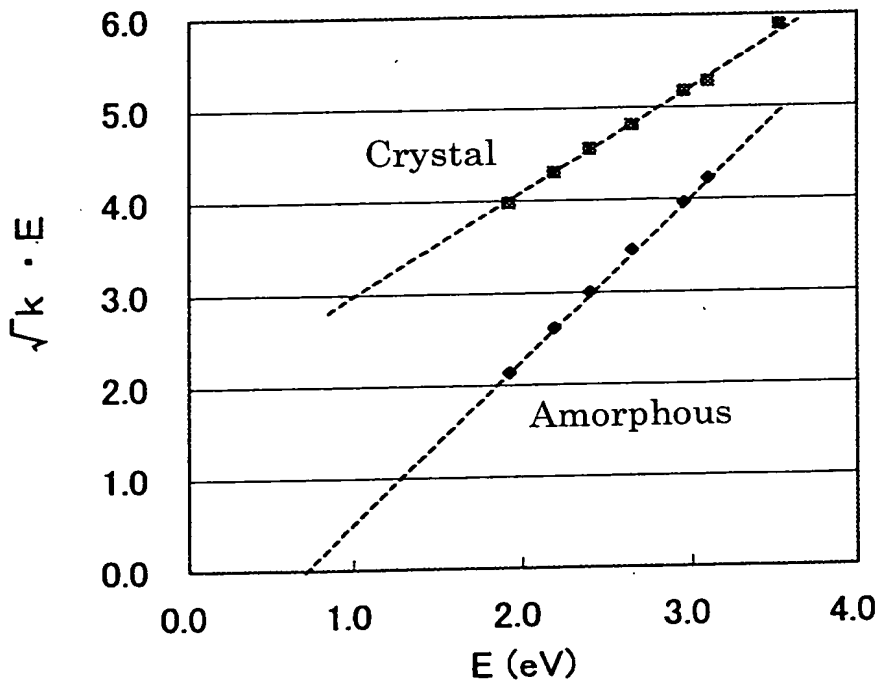


(b) Extinction coefficient

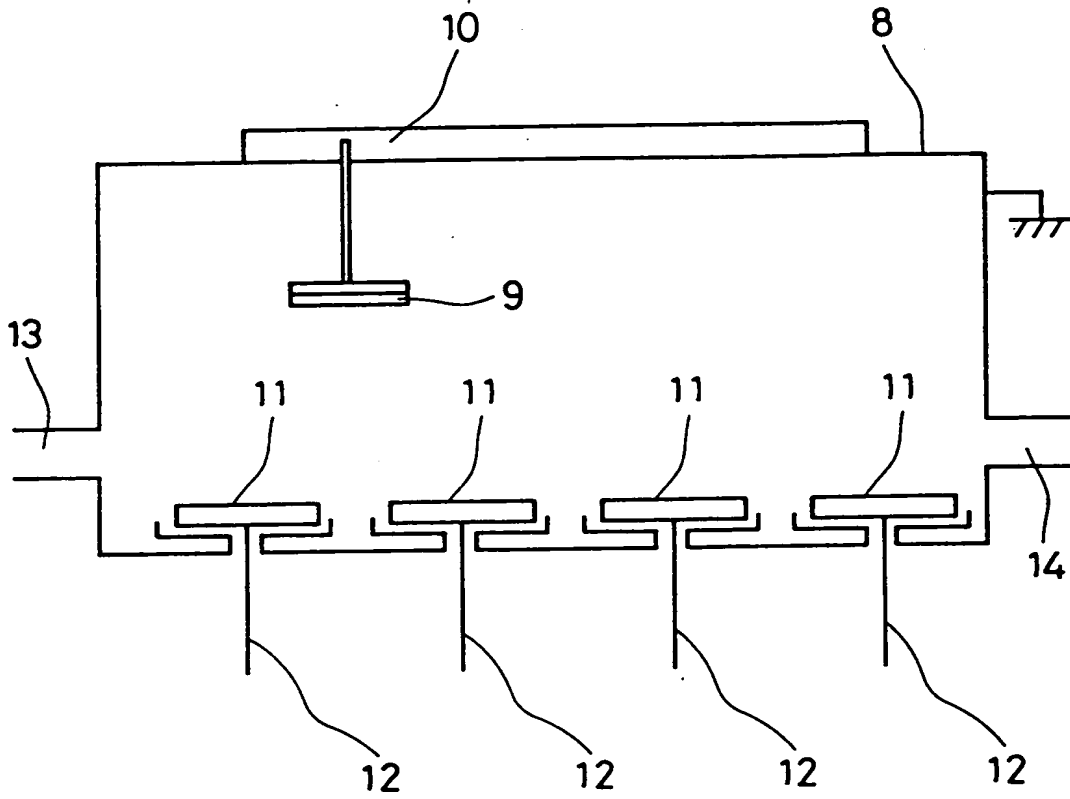
[FIG. 4]



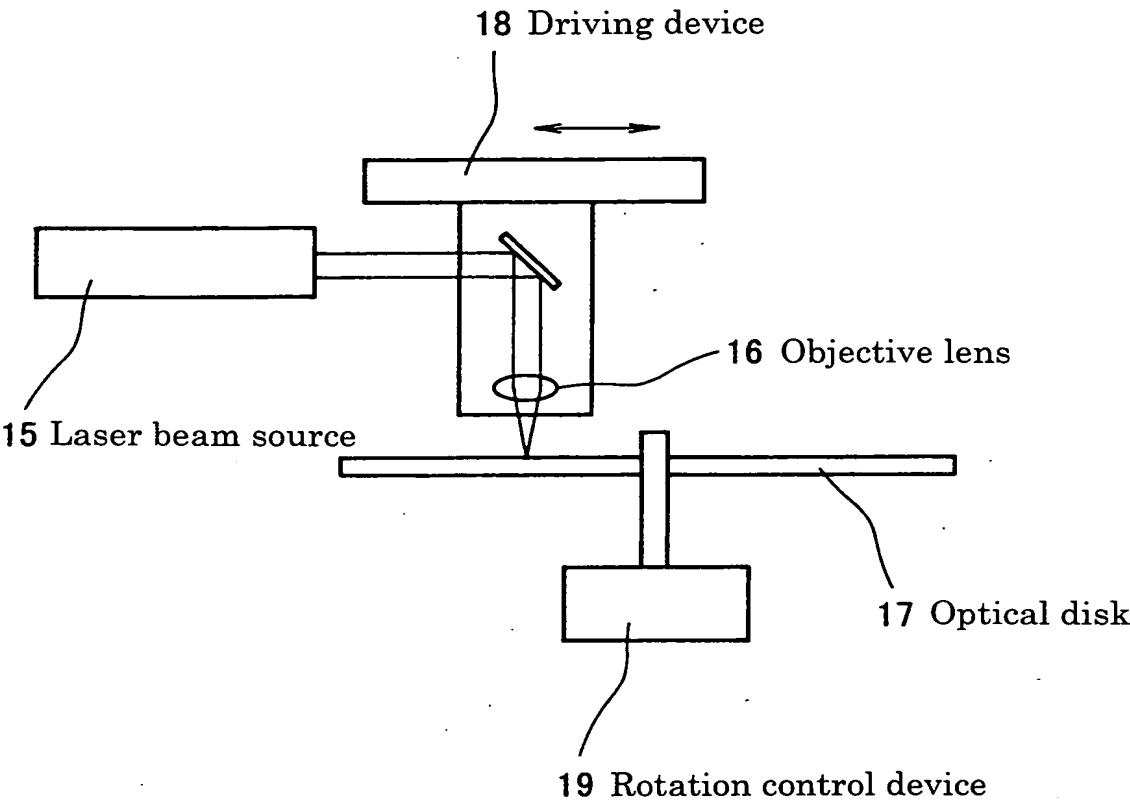
[FIG. 5]



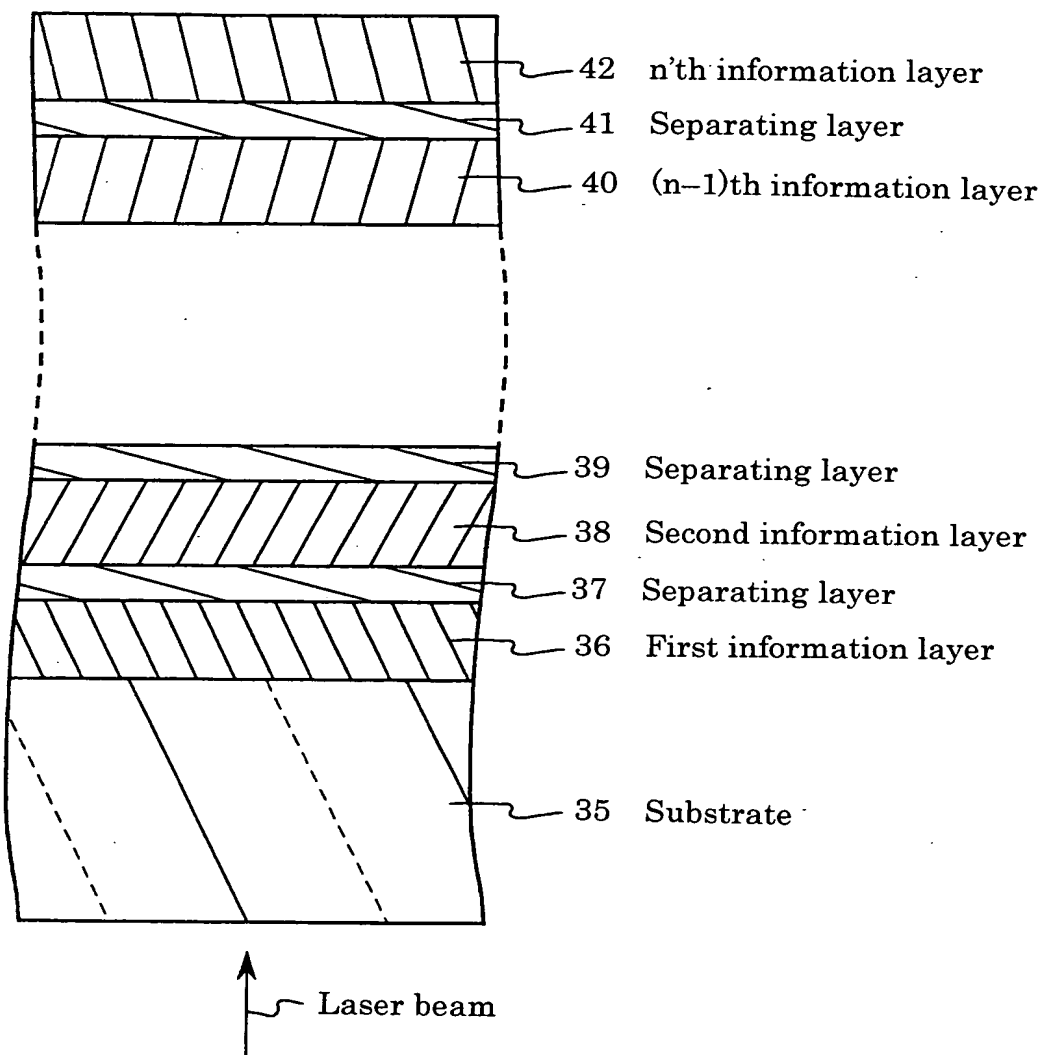
[FIG. 6]



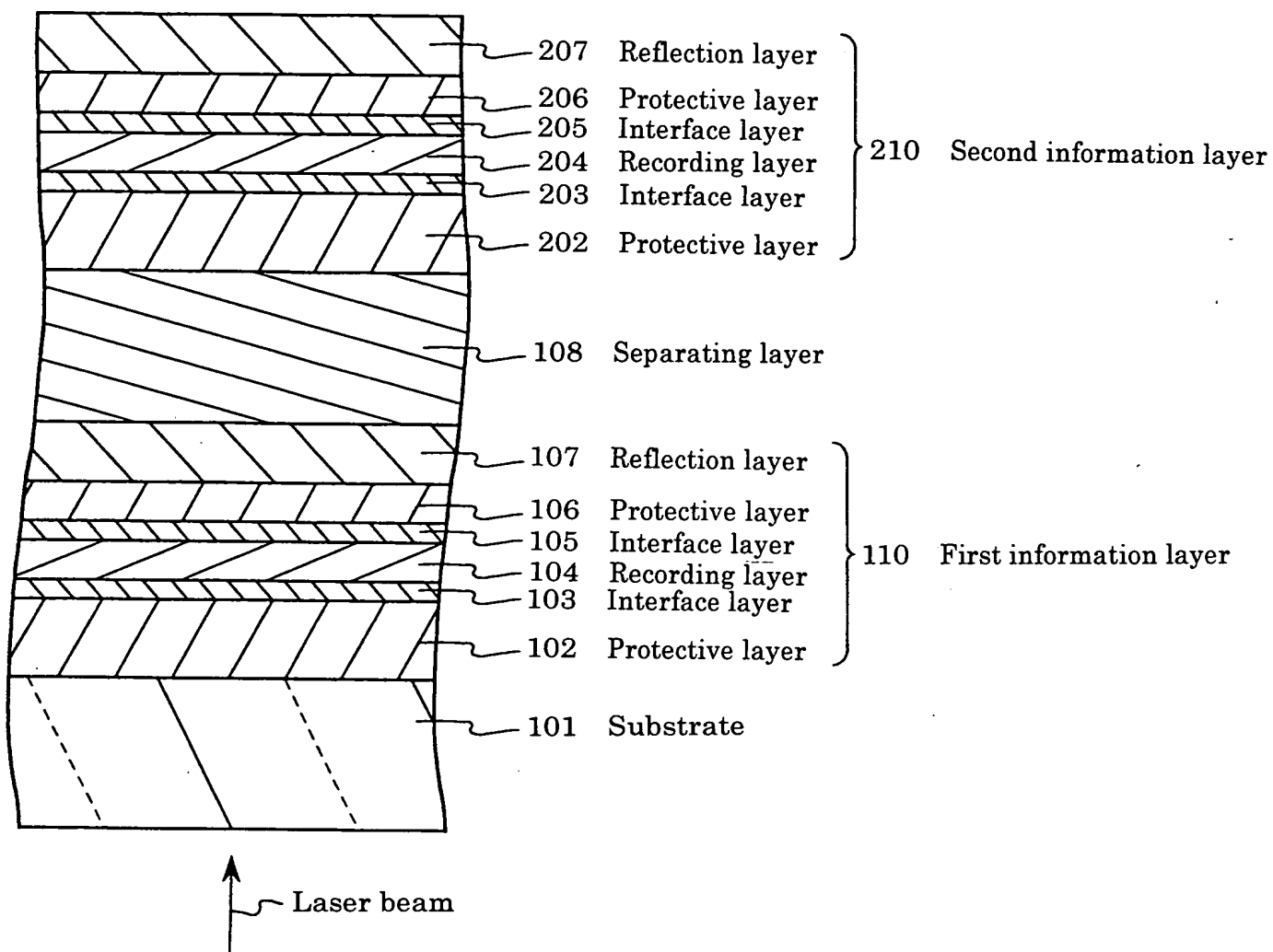
[FIG. 7]



[FIG. 8]



[FIG. 9]





[Document Name] ABSTRACT

[Abstract]

[Object] An optical information recording medium of a so-called multi-layer type using a recording material that exhibits an optimal recording characteristics when using a laser beam in the blue wavelength range is provided.

[Means to Solve the Problems] An information layer 110 including a recording layer 104 containing a material that exhibits a reversible transition between crystalline and amorphous states in response to irradiation with a laser beam as a main component is formed on a substrate 101, and this material is set to have an energy gap ranging from 0.9 eV to 2.0 eV in the amorphous state. The information layer 110 is set to have a transmittance of not less than 30% when irradiated with a laser beam with a wavelength ranging from 300 nm to 450 nm. The laser beam transmitted by the information layer 110 is irradiated onto another information layer 210. The irradiation with the laser beam from one side makes it possible to record/ reproduce information excellently in a plurality of the recording layers 104 and 204.

[Selected Figure] FIG. 9

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